

CONVERSION AND GLOBAL REACTION RATE COEFFICIENT IN THE ABSORPTION OF SO₂ BY DIFFERENT TYPES OF LIMESTONE IN A FLUIDIZED BED REACTOR

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Abstract. *This work concerns the study of the effect of limestone type on SO₂ absorption in a bench fluidized bed reactor plant. Conversion and global reaction rate coefficients were established for conditions typical to fluidized bed combustion of coal. The bench plant is a bubbling bed reactor 160 mm internal diameter using silica sand as bed material, fluidized by pre-heated air. In order to simulate conditions close to the fluidized bed coal combustion ambience, the fluidizing air is pre-heated at high temperature (850 °C) and SO₂ is added to the fluidizing air in a concentration typical of the process (1000 ppm). All the particulate, i.e. silica sand and limestone particles, was fed to the bed in a narrow size distribution between two subsequent ASTM sieves (with 545 μm mean diameter). In transient batch experiments charges of limestone are quickly injected into the bed, while the consequent variations of the exit concentrations of SO₂, CO₂ and O₂ are continuously recorded. Analysis were performed on the effects of the type of limestone in the process, taking into account possible reaction controlling resistances, and considering possible effects of the calcination on the sulfation process.*

Keywords: *fluidized bed, sulfation, sulfur absorption, limestone.*

1. Introduction

Owing to the shortage of new hydroelectric resources, Brazil is currently turning to thermal power solutions to comply with its ever growing energy requirements. Natural gas has been put forward as the main solution. About 17000 MW is predicted to be generated using this fuel along the next decade. Mineral coal is another alternative for large scale energy production. Its known reserves in Brazil can provide for up to 19000 MW for a hundred years.

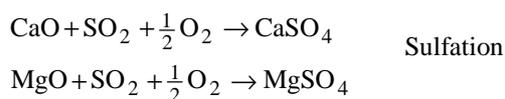
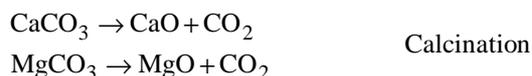
The utilization of the Brazilian coal for power generation faces some technical difficulties, mainly associated to its high contents of ash and sulfur. In the commonly applied fixed bed and pulverized coal combustion processes the emissions of SO₂ are very intense, and the inherent high temperatures cause ash fusion and high NO_x emissions. Those difficulties are overcome by applying fluidized bed combustion. The process temperatures are typically around 850 °C, thereby avoiding ash fusion and minimizing NO_x emissions. Besides, limestone is directly injected into the bed providing for *in loco* SO₂ absorption.

Most of the literature available results on SO₂ absorption in fluidized bed coal combustion stand for foreign coals and limestones. Otherwise, specific research is required for national materials since coals and limestones are very heterogeneous and present properties quite dependent on origin and geological age. In fact, even limestones coming from the same region may present quite different reaction behavior. The Group of Thermal and Fluids Engineering (NETeF) of EESC-USP is running a comprehensive research program on fluidized bed combustion of Brazilian coals. The current research is directed towards coal combustion, SO₂ absorption by limestones, and fluid mechanics of gas-solid flows. Experimental research is underway in two bubbling fluidized bed plants (pilot and bench scales), and through thermogravimetry (TGA). This work presents results from bench scale experiments on the effect of limestone type on SO₂ absorption (results on the effects of process temperature and limestone particle size can be found in Costa, 2001 and da Silva, 2001). Further results on calcination of this limestone in the bench scale fluidized bed reactor and TGA, and sulfation in TGA, can be found in Crnkovic et al. (2001). A literature review on bubbling fluidized bed combustion of high ash coals, including Brazilian coals, is presented in Milioli (1996).

Bubbling fluidized bed combustion of coals is characterized by a set of physical and chemical phenomena of very high complexity. The bubbling bed regime may be considered to be formed of two well defined hydrodynamic patterns: a particulate or emulsion phase characterized by gas dispersed particles, and a bubble phase characterized by gas voids with very few particles. So, almost all the heterogeneous reactions such as coal combustion and sulfur absorption by limestone happen in the particulate phase. The effective rates of the heterogeneous chemical reactions are controlled by chemical kinetics, and by mass transport between the bubble and the particulate phase, through the particulate phase and intraparticle.

The resistances to sulfur absorption by limestones may be either external or internal to the particles. The external resistances are related to fluidization contact phenomena such as attrition, elutriation, and mixture of gas and particulate, and related to sulfur release from coal. Limestone attrition produces fines and the wearing of the mother particles, thereby enhancing elutriation. Gas mixture determines mass transport conditions in the particulate phase, and between bubble and particulate phases. Particulate mixture exposes the limestone particles to reducing or oxidizing atmospheres, besides considerably affecting attrition and elutriation. The production of SO₂ from coal is controlled by chemical kinetics, and by transport of O₂ from bubble to particulate phase, through the particulate phase and internal to the coal particles. The internal resistances to limestone sulfation are chemical kinetics, intraparticle gas diffusion through micro, meso and macropores, gas diffusion through reacted sulfate layers and ionic diffusion. Those resistances are affected by sintering and sulfation extent.

Limestones are mostly calcium carbonate (CaCO₃). Some rocks also present significant fractions of magnesium carbonate (MgCO₃). Besides CaCO₃ and MgCO₃ a variety of impurities are present including compounds of iron, aluminum, manganese, sulfur, phosphorus, chromium and zinc, among others. As introduced in a high temperature fluidized bed the carbonates calcine to produce a very porous solid structure of CaO/MgO, which ultimately absorbs SO₂ to produce calcium/magnesium sulfate (CaSO₄/MgSO₄). The main global chemical reactions involved in the sulfation of natural limestones are:



A limestone particle comprises a collection of individual crystals or calcitic/dolomitic grains, stick in a matrix together with other crystals containing impurities. When heated, the calcitic/dolomitic crystals decompose in tiny CaO/MgO crystals tied up and connected by solid bridges. The product calcine is very porous and characterized by high internal surface areas. At higher temperatures the CaO/MgO crystals may be sinterized forming bigger crystals thereby reducing porosity and internal surface area.

In a fluidized bed combustion environment calcination is much quicker than sulfation. At a given moment a particle would be completely calcined as sulfation proceeds. SO₂ diffuses through the calcined particle percolating along the boundaries between grains and internal cracks. It is then absorbed at the CaO/MgO crystal surfaces where chemical reaction occurs. As sulfation goes on the product CaSO₄/MgSO₄ expand in comparison to the original CaO/MgO crystals causing porosity reduction. The pores finer and closer to the particle surface, and the corresponding surface areas, are predominantly exposed to sulfation. At a given moment the particle would be completely pore plugged by the product sulfates throughout its layer closer to the external surface, and its core would be virtually inaccessible to reaction. In such a situation the only remaining routes for chemical reaction would be the very slow mass and ionic diffusion through the sulfate layers. For practical purposes, pore plugging ultimately limits sulfur absorption.

In general, below 800 °C chemical reactions are slow and chemical kinetics controls sulfur absorption by limestones in bubbling fluidized bed coal combustion. Between 800 and 900 °C chemical reaction becomes faster and mass diffusion takes control of the process. Above 900 °C the product calcium sulfate becomes unstable and decomposes releasing SO₂. This behavior suggests there are optimal operational temperatures for what the reaction efficiency is maximum. In real scale plant operation under coal combustion and continuous feeding such temperature is commonly found between 800 and 850 °C, where absorption of SO₂ exceeds 90% (Howard, 1989).

The maximum theoretical conversion of a limestone particle concerning sulfur absorption is supposed to be of about 50%. Such a level would be reached when all the pores of the rock are filled with sulfate. However, pore plugging at the external layers of the particles, owing to the higher molar volume of the sulfates compared to that of calcium oxide, prevents conversion to reach the 50% figure, and in practice much lower values are found (Yates, 1983).

Sulfur absorption by limestone in coal fluidized bed combustion has been approached by different procedures, including or not coal combustion, either in batch or continuous reaction experiments. Despite experiments under coal combustion are better representative of the real process, the unknown reactive atmosphere greatly difficult comparison among different researches. On the other hand, experiments simulating combustion conditions allow a better control and comparability. In these cases, caution is required when evaluating results since in general there are considerable differences between the real processes and the simulations. Continuous experiments are usually performed in large units, while batch experiments are more commonly performed in small scale units. While continuous experiments are

more realistic, batch experiments are more flexible, allowing analysis of the limestone transient absorption performance.

Literature presents a great amount of works on limestone calcination and sulfation in different experimental rigs, including thermogravimetric analysers, crucible, differential and entrained flow reactors, fixed and fluidized bed reactors. A discussion is presented next accounting for experiments developed at conditions close to typical fluidized bed combustion of coals, either simulated or not, and mainly concerning the effects of the type of limestone on calcination and sulfation.

Borgwardt (1985) studied calcination of two limestones of different geological ages. The process was developed in differential and entrained flow reactors, at temperatures up to 1000 °C. Results showed that calcination kinetics was independent of limestone type. When intra and interparticle mass transfer are eliminated, calcination rate is directly correlated to the BET surface area of the limestone. In a continuing work, Borgwardt, Bruce and Blake (1987) studied sulfation at 800 °C of absorbents produced from the calcination of $\text{Ca}(\text{OH})_2$ and CaCO_3 . The absorbent produced from $\text{Ca}(\text{OH})_2$ was more effective, owing to a better grain expansion during calcination and a consequent higher BET surface area. Stouffer and Yoon (1989) studied sulfation of limestones in a differential reactor at temperatures between 700 and 1000 °C. Seven types of limestone, two types of dolomite and two CaO hydrated absorbents were used. They found that sulfation rate is limited by diffusion of SO_2 through pores, thereby concluding that porosity generated during calcination, quite different for the various sorbents, is a key factor. The hydrated CaO showed better performance as compared to the other absorbents.

Khinast et al. (1996) carried out thermogravimetric calcination experiments in CO_2/N_2 atmospheres at 780 °C. They found that reaction rate is considerably affected by particles texture, and is controlled by chemical kinetics and intraparticle mass diffusion. Krishnan and Sotirchos (1993) performed sulfation of three different limestones in a thermogravimetric analyzer at temperatures of 750 and 850 °C. The atmospheres were CO_2/air for the calcination step and $\text{SO}_2/\text{CO}_2/\text{air}$ for the sulfation step. The petrography of the limestones was found to play a significant role concerning absorption efficiency since it is directly related to porosity and pore size of the calcine.

Borgwardt and Harvey (1972) studied sulfation of several different limestones in a differential reactor, at 980 °C. For all the different limestones, they found that the size distribution and the volume of pores developed during calcination critically affect sulfur absorption. Bathia and Perlmutter (1981) reached the same conclusions.

Most of the works in the literature assume calcination as instantaneous, including Dennis and Hayhurst (1986, 1988) and Mattisson and Lyngfelt (1988). Haji-Sulaiman and Scaroni (1992) performed batch experiments of sulfur absorption by limestone in a bed fluidized by a pre-heated mixture of SO_2 , CO_2 , O_2 and N_2 . Four different limestones were used, at temperatures from 750 to 935 °C. They found that the calcination step was not instantaneous. The observed different behaviors of the different limestones were attributed to impurities and chemical composition. In general impurities reduce the decomposition temperature and raise the initial reaction rate. Some impurities were found to affect the physical structure of the limestones during calcination.

Carello and Vilela (1993) carried out sulfation in a thermogravimetric analyzer of five types of limestone. The experiments were performed at 850 °C in atmospheres of pure SO_2 . They found that higher contents of MgO do not improve the efficiency of the absorbent, and that the calcitic limestones were more reactive.

Dam-Johansen and Ostergaard (1991) studied sulfur absorption by various limestones of different geological ages through batch experiments in a recycle reactor, a bench fluidized bed reactor, and a coal fired fluidized bed pilot plant. They found that the capacity for sulfur absorption of the limestones in all the systems is closely correlated to physical texture, and then to geological age. The young geological age limestones, which are very porous, were far more reactive than old geological age limestones, which are very compact. They also found that the presence of ferric oxide considerably enhances sulfation. Except for ferric oxide, no other effect of chemical composition was observed. Concerning sulfur absorption, the relative ranking between the limestones is nearly the same in all the three systems.

Mattisson and Lyngfelt (1999) developed fluidized bed batch experiments for sulfur absorption by three different limestones in fluidized bed simulated conditions. Charges of limestone were exposed to atmospheres of SO_2 , O_2 , CO_2 and N_2 , at temperatures between 825 and 875 °C. The authors observed that at low temperatures the sulfation was limited by incomplete calcination, while at sufficiently high temperatures the limitation was due to SO_2 re-emission.

Lyngfelt and Leckner (1989) studied sulfur absorption by limestone in a 16 MW bubbling fluidized bed boiler under coal combustion. They found that at 930 °C there was re-emission of SO_2 from sulfated limestone. Leckner et al. (1992) studied sulfur emission in two bubbling fluidized bed boilers, of 40 and 160 MW, under coal combustion. They considered two different limestones and a process temperature of 850 °C. They found no effect of limestone type on sulfur absorption.

Dennis and Hayhurst (1986 and 1990) developed batch experiments of sulfur absorption by limestone in a bubbling fluidized bed at temperatures from 750 to 975 °C, under an atmosphere of SO_2 , O_2 and N_2 . They observed that below 650 °C the conversion must be limited by the formation of CaSO_4 layers on the reactive surfaces. Above 650 °C pore plugging limits absorption.

The several experiments differ to each other as for limestone type, reaction conditions and scale. Bubbling fluidized bed reactor of very small cross section have been used in batch experiments, imposing flow conditions greatly deviated from the real large scale process. In this work a 160 mm i.d. bubbling bed is used, which is larger than any other batch reactor appearing in the literature.

2. Theory

In this work sulfur absorption is determined through batch experiments. The efficiency of absorption is addressed through the literature commonly used definitions of conversion and global reaction rate coefficient. A global mass balance for the SO₂ in the process results

$$\frac{dX(t)}{dt} = \frac{1}{M_L \left(\frac{Y_{Ca}}{W_{Ca}} + \frac{Y_{Mg}}{W_{Mg}} \right)} U A C_{SO_2}^e \left[1 - \frac{C_{SO_2}^s(t)}{C_{SO_2}^e} \right] \quad (1)$$

where $X(t)$ is the conversion defined as the molar quantity of SO₂ absorbed by mol of CaO/MgO injected into the process. Integrating the above expression from the moment of limestone injection until a given residence time t , the conversion results

$$X(t) = \frac{1}{M_L \left(\frac{Y_{Ca}}{W_{Ca}} + \frac{Y_{Mg}}{W_{Mg}} \right)} U A C_{SO_2}^e \int_0^t \left[1 - \frac{C_{SO_2}^s(t)}{C_{SO_2}^e} \right] dt \quad (2)$$

Limestone consumption may be expressed as

$$R_A(t) = U A \left[C_{SO_2}^e - C_{SO_2}^s(t) \right] \quad (3)$$

Another expression for limestone consumption may be established as a function of a global reaction rate coefficient. For that, a set of assumptions must be made. Limestone particles are assumed spherical and well characterized by the mean diameter. Particle size and density are assumed not to change during the process. Mass transport in the emulsion phase is assumed to occur by diffusion following Fick's law. The concentration of SO₂ in the emulsion phase far from a limestone particle surface is assumed constant and uniform. Following the above, limestone consumption results

$$R_A(t) = \frac{6M_L}{d_L \rho_L} K_A C_{SO_2}^p \quad (4)$$

where the global reaction rate coefficient, K_A , takes into account resistances to reaction due to external gas mass transfer, chemical kinetics, and intraparticle gas diffusion. Combining Eqs. (3) and (4), the global reaction rate coefficient results

$$K_A = \frac{\rho_L d_L}{6M_L} U A \left[\frac{C_{SO_2}^e - C_{SO_2}^s(t)}{C_{SO_2}^p} \right] \quad (5)$$

The concentration of SO₂ in the emulsion phase, $C_{SO_2}^p$, is determined following the literature well known Orcutt's model (see, for instance, Grace, 1986). The procedure follows the classical two-phase theory of fluidization of Toomey and Johnstone (1952). The emulsion phase is assumed well mixed, and the bubble phase is assumed in plug flow. No absorption of SO₂ is assumed to occur in the bubble phase since all limestone particles are considered to remain in the emulsion phase all the time. The bubble phase is assumed to be well characterized by bubble's mean volume, diameter and velocity. The bulk mass transport between bubble and emulsion phases is assumed to be governed by a constant mass transfer coefficient. Following the above assumptions it is found that

$$C_{SO_2}^p = \frac{\left[1 - \frac{C_{SO_2}^e}{C_{SO_2}^s(t)} \left(1 - \frac{U_{mf}}{U} \right) \exp(-\chi) \right]}{\left[1 - \left(1 - \frac{U_{mf}}{U} \right) \exp(-\chi) \right]} C_{SO_2}^s(t) \quad (6)$$

The global reaction rate coefficient results

$$K_A = \frac{\frac{\rho_L d_L}{6M_L} UA \left[\frac{C_{SO_2}^e}{C_{SO_2}^s(t)} - 1 \right] \left[1 - \left(1 - \frac{U_{mf}}{U} \right) \exp(-\chi) \right]}{\left[1 - \frac{C_{SO_2}^e}{C_{SO_2}^s(t)} \left(1 - \frac{U_{mf}}{U} \right) \exp(-\chi) \right]} \quad (7)$$

Several parameters are required for solving Eqs. (1) to (7). Literature commonly used correlations are assumed which are listed in Tab. (1).

Table 1. Correlations for some required parameters.

Minimum fluidizing velocity (Wen and Yu, 1966)	
$U_{mf} = \frac{\mu_g}{d_v \rho_g} \left[(1135.7 + 0.0408Ar)^{0.5} - 33.7 \right]$	(8)
where	
$Ar = \frac{\rho_g d_v^3 (\rho_p - \rho_g) g}{\mu_g^2}$	(9)
$d_v = 1.13d_p \quad (\text{Geldart, 1986})$	(10)
Bed voidage at minimum fluidizing conditions (Wen and Yu, 1966)	
$\varepsilon_{mf} \approx 1 - \left(\frac{11}{14} \right) \phi$	(11)
Height of the bed at minimum fluidizing conditions (Geldart, 1986)	
$H_{mf} = \frac{M}{\rho_p A (1 - \varepsilon_{mf})}$	(12)
Height of the expanded bed (Babu et al., 1978)	
$H = H_{mf} \left[1 + \frac{14.314(U - U_{mf})^{0.738} (d_p)^{1.006} (\rho_p)^{0.376}}{(U_{mf})^{0.937} (\rho_g)^{0.126}} \right]$	(13)
Bubble rising velocity (Davidson and Harrison, 1963)	
$U_b = U - U_{mf} + 0.711\sqrt{gd_b}$	(14)
Bubble diameter (Darton et al., 1977, Stubington et al., 1984)	
$d_b = 0.239(U - U_{mf})^{0.4} \left[(H + 0.1272)^{1.8} - 0.0244 \right] g^{-0.2} H^{-1}$	(15)
Cross flow factor, i.e. non-dimensional gas mass transfer coefficient between bubble and particulate phases, (Davidson and Harrison, 1963)	
$\chi = \frac{K_{bp} H}{U_b V_b} = \frac{6.34 H_{mf}}{d_b (gd_b)^{0.5}} \left(U_{mf} + \frac{1.3 \varepsilon_{mf} D_G^{0.5} g^{0.25}}{(1 + \varepsilon_{mf}) d_b^{0.25}} \right)$	(16)

In Eqs. (1) to (16):

- A Bed cross sectional area, m²
- Ar Number of Archimedes, non-dimensional
- C_{SO₂}^e Entrance concentration of SO₂, kmol/m³
- C_{SO₂}^p Concentration of SO₂ in the emulsion phase, kmol/m³
- C_{SO₂}^s Exit concentration of SO₂, kmol/m³
- d_b Bubble diameter, m
- d_L Limestone particle mean diameter, m

d_p	Particle mean diameter in the bed, m
d_v	Particle volumetric mean diameter in the bed, m
D_G	Gas molecular diffusion coefficient, m^2/s
$\frac{dX}{dt}$	Limestone conversion rate, $kmol(SO_2)/kmol(Ca+Mg).s$
g	Gravity acceleration, m/s
H	Expanded bed height, m
H_{mf}	Bed height at minimum fluidizing conditions, m
K_A	Global reaction rate coefficient, m/s
K_{bp}	Gas mass transfer coefficient between bubble and emulsion phases, m^3/s
M	Mass of the bed, kg
M_L	Batch of limestone, kg
R_A	Limestone consumption, $kmol(Ca+Mg)/s$
r	Limestone particle radius, m
t	Time, s
U	Superficial fluidizing velocity, m/s
U_b	Bubble velocity, m/s
U_{mf}	Minimum fluidizing velocity, m/s
V_b	Bubble volume, m^3
W	Molecular weight, $kg/kmol$
X	Limestone conversion, $kmol(SO_2)/kmol(Ca+Mg)$
Y	Mass fraction, non-dimensional
ε_{mf}	Bed voidage at minimum fluidizing conditions, non-dimensional
μ_g	Gas viscosity, $kg/m.s$
ρ_g	Gas density, kg/m^3
ρ_L	Limestone particles density, kg/m^3
ρ_p	Bed particulate density, kg/m^3
Φ	Particle sphericity factor, non-dimensional
χ	Cross flow factor, non-dimensional

3. Experiment

The basic experiment consists of fluidizing a bed of silica sand particles with pre-heated air at controlled temperatures. In order to simulate sulfur generated in coal fluidized bed combustion, SO_2 is added to the fluidizing air in a concentration typical of the process. In the transient batch experiments charges of limestone are quickly injected into the bed, while the consequent variations of the exit concentrations of SO_2 , CO_2 , and O_2 are continuously measured in Horiba Enda 1400 gas analyzers.

Figure (1) shows a sketch of the bench scale fluidized bed plant used in the experiments. The reactor is an atmospheric bubbling fluidized bed with 160 mm of internal diameter. SO_2 is homogeneously mixed into the air after heating. A cyclone is used for particulate retention. Continuous gas sampling is carried out at the cyclone exit. Comprehensive descriptions of the plant can be found in Costa (2000), Camargo (2001) and da Silva (2001).

The bed material was about 2.8 kg of silica sand, with injected charges of limestone of about 50 g. Both silica sand and limestone particulate were 545 μm mean diameter, selected in narrow size distributions between the subsequent 500-590 μm ASTM sieves. The experiments were carried out at 850 °C under bubbling fluidized bed conditions, at a superficial velocity 4 times the minimum fluidizing velocity, i.e. about 0.41 m/s. The expanded bed height resulted about 95 mm. The SO_2 injected with the fluidizing air resulted in initial exit concentrations, before the injection of limestone, close to 1000 ppm.

Five different types of limestone were used, whose partial chemical compositions are presented in Tab. (2). According to the MgO content of the calcined rock limestones can be classified in either calcitic (0 to 1.1% MgO), magnesian (1.1 to 2.1% MgO) or dolomitic (2.1 to 10.8% MgO) (Pettijohn, 1957). Regarding geological age limestones can be classified in either old (1.0 to 1.8 billion years), intermediary (435 to 570 million years) or young (230 to 251 million years) (Abreu, 1973). Limestones named 1-Ci, 1-Mi and 1-Di come from Itaú de Minas (MG), are respectively calcitic, magnesian and dolomitic, and are all old aged metamorphic rocks. Limestone 1-Cs comes from São José da Lapa (MG), and is a calcitic intermediary aged sedimentary rock. Limestone 1-Dp comes from Piracicaba (SP), and is a young aged sedimentary rock.

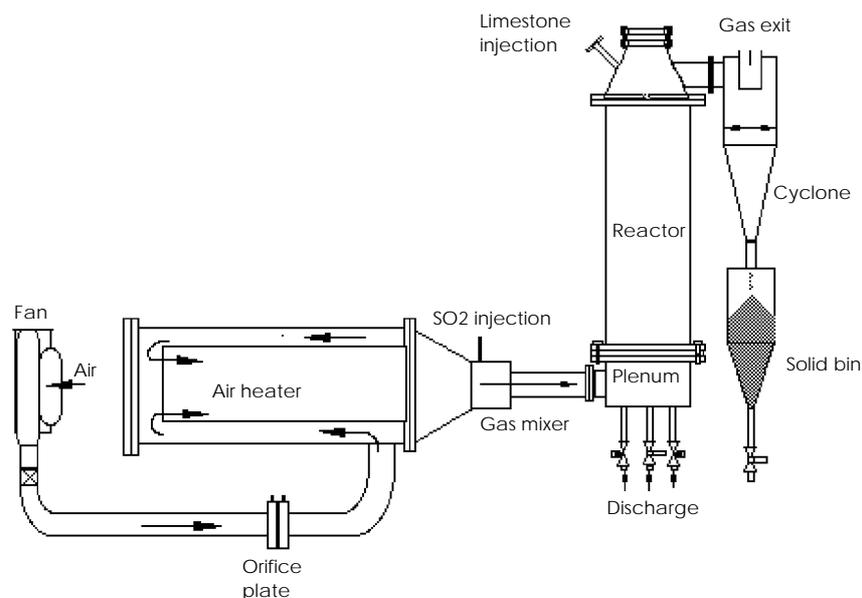


Figure 1. Sketch of the bench scale fluidized bed plant.

Table 2. Partial elemental chemical composition of the limestones (mass %).

Limestone	Sr	Mn	Ba	K	P	Fe	Al	Ca	Mg
1-Ci	0.1346	0.03915	0.00095	0.0607	0.0099	0.0989	0.1675	38.5	1.007
1-Mi	0.097	0.039	0.0016	0.062	0.1804	0.1876	0.1057	28.83	4.1927
1-Di	0.017	0.0068	0.00224	0.113	0	0.2269	0.076	23.2568	9.3298
1-Cs	0.3415	0.00796	0.0038	0.1036	0.08224	0.12835	0.1797	32.717	0
1-Dp	0.0811	0.0888	0.0054	0.097	0.0554	0.3207	0.4233	17.07	11.727

4. Results and discussion

Figure (2) shows the transient concentration of SO_2 for the sulfation of the five different limestones. As seen, shortly after limestone injection the concentration of SO_2 sharply drops to a very low level for all the limestones. In all the cases the reactivity of the particles is progressively reduced and SO_2 concentration tends to recover to its initial value. The younger limestone 1-DP is much more effective compared to the others for it keeps absorbing SO_2 for a much longer period of time. The older limestones 1-Ci, 1-Mi and 1-Di as well as the middle aged limestone 1-Cs present similar performances, which are far less than that of the limestone 1-Dp.

Figures (3), (4) and (5) present, respectively, conversion, conversion rate and global reaction rate coefficient for all the limestones. In agreement with the SO_2 transient concentration profile, limestone 1-DP reaches a much greater conversion than any other limestone, which is seen in Fig. (3). The lowest level of conversion is reached by limestone 1-Ci. The conversion rate depicted in Fig. (4) shows a very steep conversion gradient for all the old and middle aged limestones, quickly tending to a very low level after about 3000 seconds of reaction. Such a low level is not reached for limestone 1-Dp even above 8000 seconds of reaction. Conversion gradient for limestone 1-Dp changes very slowly, showing that the particulate keeps highly reactive for a long period of time. The global reaction rate coefficient showed in Fig. (5) reaches much higher values for limestone 1-DP compared to the other limestones. Not only the initial value is much higher, but also the gradient of the coefficient in time is much slower, again indicating the superior reactivity of limestone 1-DP. For the older and middle aged limestones the global reaction rate coefficient drops one order in a minute in a very sharp rate, and continues to decrease afterwards at lower and lower rates. The decreasing rates of both conversion and global reaction rate coefficient indicate a switch of the reaction controlling mechanism from chemical kinetics to intraparticle gas diffusion.

The factor or factors explaining the better performance of limestone 1-Dp may be related to either a more suitable porosity developed on calcination, a possible incomplete calcination of the other limestones or different catalytic effects of composition elements.

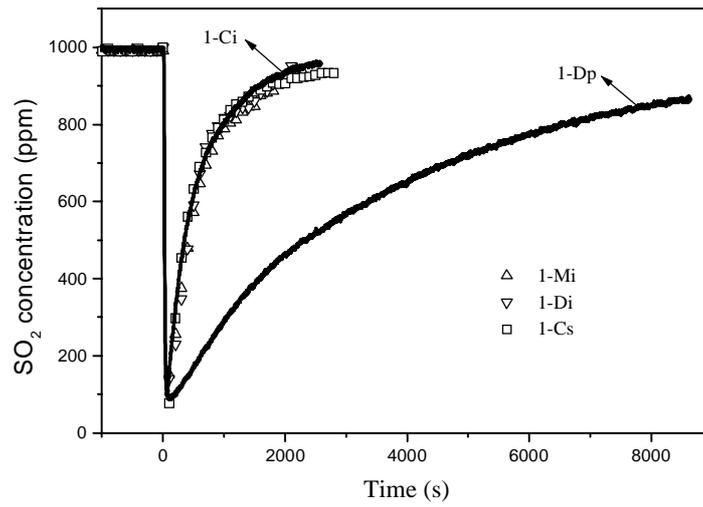


Figure 2. Exit transient concentration profiles of SO_2 .

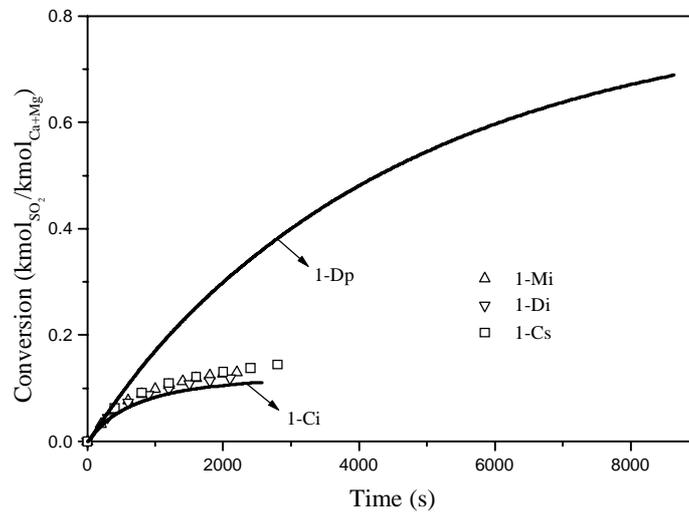


Figure 3. Limestone conversion.

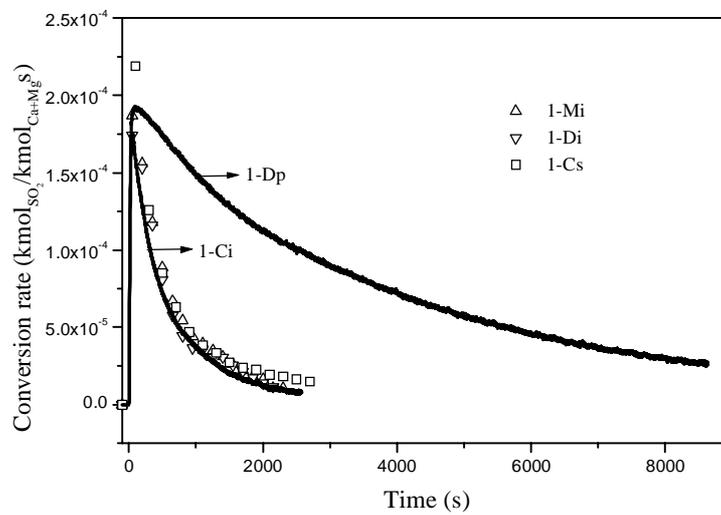


Figure 4. Limestone conversion rate.

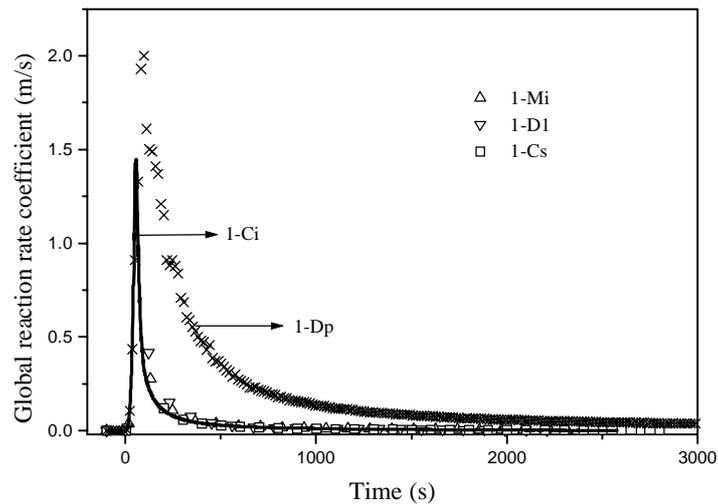


Figure 5. Global reaction rate coefficient.

The possibility of incomplete calcination for justifying a lower sulfation is ruled out by the results of CO₂ emissions. Figure (6) shows CO₂ emissions during calcination. The integral over the CO₂ concentration profile gives the amount of the released gas, and results approximately equal for all the limestones. Also, the carbon contents of the limestones are very close (as inferred from Ca and Mg contents, supposing that all C is present as CaCO₃ and MgCO₃). The above suggests that calcination proceeds at a similar extent for all the limestones. It seems reasonable to assume that, if calcination extent does not impose a low reactivity for limestone 1-Dp, it should not impose a low reactivity for any of the other limestones. Therefore, calcination extent does not seem to be a major cause for low reactivity. The transient concentrations of O₂ presented in Fig. (7) confirm the correctness of the results on CO₂ concentrations. The dilution effect caused on O₂ concentration due to CO₂ production during calcination is clearly seen.

Chemical composition giving rise to catalytic effects could explain the different behavior of the limestones. As seen in Tab. (1), many elements found in limestone 1-Dp are also present in the other limestones. Nevertheless, the elemental analysis is partial and must be approached with caution. Even though the Ca plus Mg content is similar for all the rocks, limestone 1-DP presents less Ca and more Mg than any other limestone. Further studies are required on those matters.

Otherwise, the better performance of limestone 1-Dp may be a consequence of a pore structure more favorable to sulfation. Pore plugging may advance in a much stronger way for the older limestones possibly owing to a finer pore structure generated during calcination. About 50 seconds are required for the calcination of limestone 1-Dp, while about 100 seconds is required for all the other limestones. The way that calcination velocity affects porosity is not known. Also, calcination and sulfation come along simultaneously as far as calcination persists. The way that sulfation affects calcination and the consequent calcine porosity is not clear. The above aspects are under current investigation at NETeF, mainly regarding limestones 1-Ci (the less reactive) and 1-Dp (the more reactive).

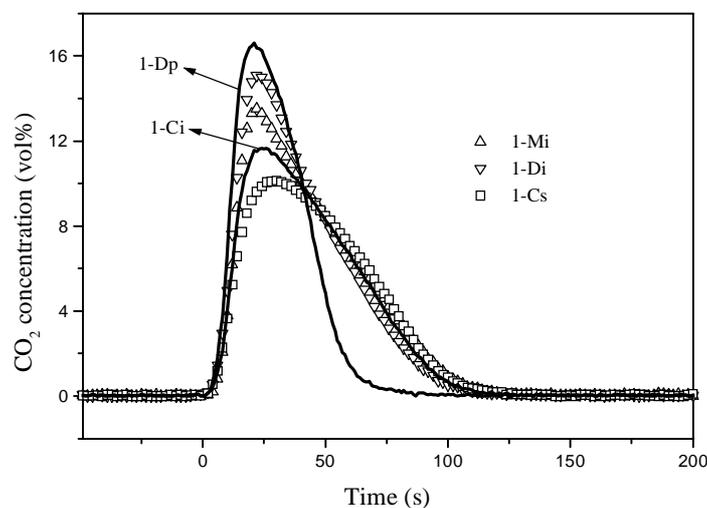


Figure 6. Exit transient concentration profiles of CO₂.

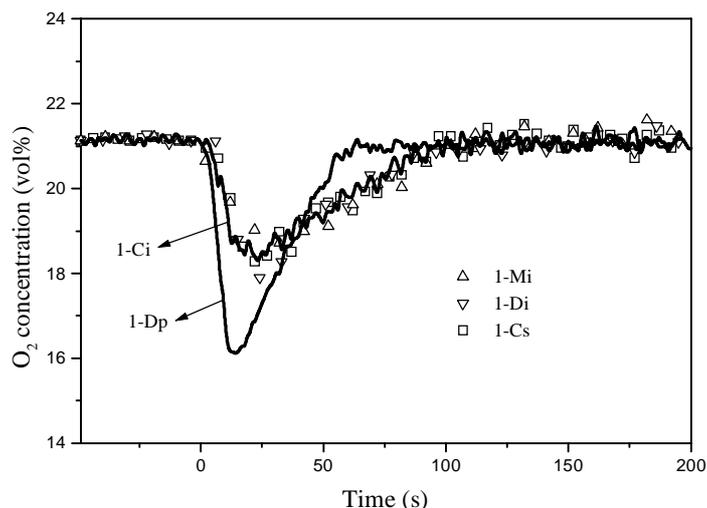


Figure 7. Exit transient concentration profiles of O₂.

5. Conclusions

Sulfur absorption by different types of limestone was studied for bubbling fluidized bed coal combustion simulated conditions. The 160 mm i.d. reactor that was used is larger than any other batch reactor appearing in the literature. Calcination was showed not to be instantaneous, so that sulfation and calcination develop simultaneously for a considerable period of time. Effects of calcination over sulfation and a switch between chemical kinetics and gas diffusion chemical reaction control were observed.

A clear effect of geological age was observed regarding limestone capability for sulfur removal. The younger limestone 1-Dp was much more reactive than the older limestones 1-Ci, 1-Mi and 1-Di and the middle aged limestone 1-Cs. Possible explanations for such a behavior were considered. Incomplete calcination as a cause for low sulfation was ruled out since the total emission of CO₂ compared to the carbon content of the rock is similar for all the limestones, including limestone 1-Dp. It was acknowledged that the better performance of limestone 1-Dp might be a consequence of a pore structure more favorable to sulfation, and that catalytic effects of elements should not be disregarded. The above trends are under current investigation at NETeF, mainly regarding limestones 1-Ci (the less reactive) and 1-Dp (the more reactive).

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